A New Home for Greenhouse Gases

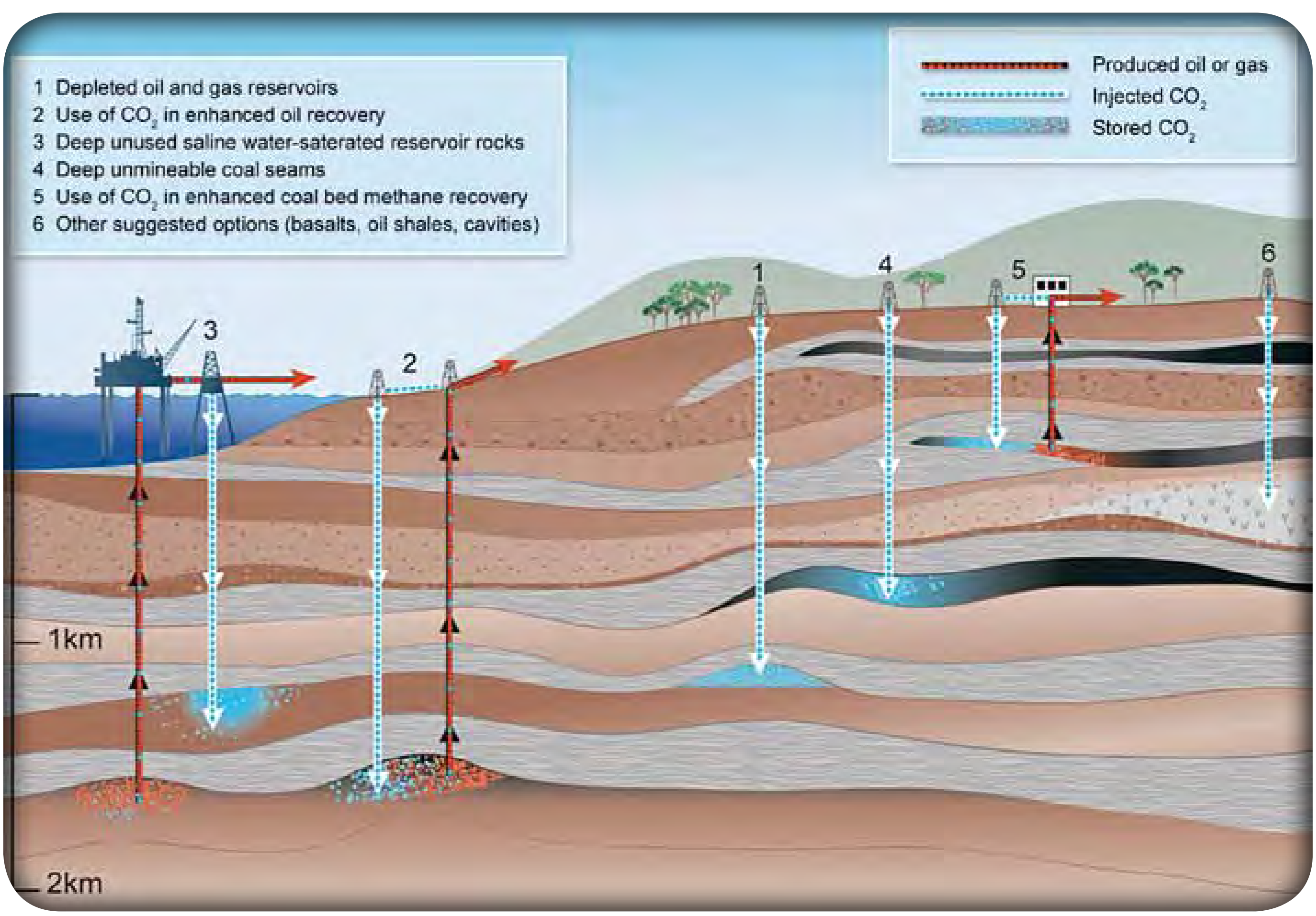
Small-angle and quasielastic neutron scattering map pores for future CO_2 capture and storage.

ONE PROPOSAL FOR ARRESTING THE RISING CONCENTRATION OF ATMOSPHERIC CO_2 IS CARBON CAPture and sequestration in underground natural porous media (saline aquifers, depleted oil and gas reservoirs, and unmineable coal seams). The amount of CO_2 that can be adsorbed by a coal or other porous material is one of the critical parameters for sequestration technology. However, no existing experimental method is yet competent to help researchers understand and predict fluid adsorption capacities in various coals.

For this purpose, researchers led by Yuri Melnichenko of ORNL have used SANS, ultrasmall-angle neutron scattering (USANS), and QENS to assess quantitative, pore-size-specific information on the sorption and mobility of CO_2 into the microstructure of various coal types. The group has developed unique high-pressure cells so that neutron scattering can register scattering patterns over a wide range of scattering angles, at temperature and pressure that correspond to underground conditions in coal seams with a depth down to 10 km below sea level.

The team also developed a novel way to interpret SANS and USANS data that allows them to “look inside” pores and to obtain pore-size-specific information about how well the micro-, meso-, and macropores of coal adsorb CO_2. (1) The advantage over traditional sorption measurements is that small-angle scattering can distinguish the contribution of different pore sizes to the total adsorption phenomenon. The method can be used to study the fluid behavior in any natural or engineered porous system with polymeric, carbon, or inorganic membranes.

SANS and USANS experiments using the methodology developed by the team have revealed unexpected results, such as strong densification of CO_2 in micro- and mesopores of coal (up to a factor of five), which could not be predicted from exist-



Geological storage options for CO_2.

ing models. At the same time, QENS experiments done on BASIS at SNS reveal a dramatic decrease of methane diffusivity in small pores (more than two orders of magnitude), compared with bulk coal (2). Such results demonstrate that small pores work as a “molecular pump” that condenses confined greenhouse gases into liquid.

Accurate interpretation of the scattering from CO_2-saturated rocks requires parallel studies of fluid adsorption in model systems such as porous fractal silica, with known composition and controllable structure. In another 2010 study, researchers used the SANS instrument to monitor CO_2 in pores of different sizes in porous fractal silica and silica aerogel (3,4). The work furthers understanding of the phase behavior of confined fluids, which is of interest for a variety of technologies, including CO_2 sequestration and enhanced coal bed methane (ECBM) recovery technologies.

It is a complex task to establish quantitative relationships between the microstructure and matrix chemistry of a porous solid and the accessibility of its pore space to an invading fluid in an arbitrary thermodynamic state. The methodology described here may be used for in situ quantification of coal pores accessible to CO_2 and methane at temperatures and pressures corresponding to subsurface conditions. Such experiments help to refine existing methods used for calculating sorption capacity of subsurface gas reservoirs and to improve the models used for evaluating the kinetics of methane production from coal seams. Such work provides essential information for ECBM technologies and geological storage of anthropogenic carbon.

This work was performed at the General-Purpose SANS instrument at HFIR, BASIS at SNS, and the BT-5 Double-Crystal Diffractometer at the National Institute of Standards and Technology (NIST). Some of this research also concerns the Illinois Basin CO_2 Sequestration Regional Partnership activity, funded by DOE. The publication of these results has attracted the widespread attention of the Geology and CO_2 sequestration communities and was highlighted in *Chemical & Engineering News (5)*.

References

1. A. P. Radliński, T. L. Busbridge, E. MacA. Gray, T. P. Blach, G. Cheng, Y. B. Melnichenko, D. J. Cookson, M. Mastalerz, and J. Esterle, “Dynamic micromapping of CO_2 sorption in coal,” *Langmuir* **25**, 2385 (2009).

2. S. M. Chathoth, E. Mamontov, Y. B. Melnichenko, and M. Zamponi, “Diffusion and adsorption of methane confined in nano-porous carbon aerogel: A combined quasi-elastic and small-angle neutron scattering study,” *Microporous Mesoporous Mater.* **132**, 148 (2010).

3. Y. B. Melnichenko, H. Mayama, G. Cheng, and T. Blach, “Monitoring phase behaviour of sub- and supercritical CO_2 confined in porous fractal silica with 85% porosity,” *Langmuir* **26**, 6374 (2010).

4. S. Ciccariello, Y. B. Melnichenko, and L. He, “Supercritical carbon dioxide behavior in porous silica aerogel,” *J. Appl. Cryst.* **44**, 43 (2011).

5. J. N. Kemsley, “Making use of neutrons,” *Chem. Eng. News* **88**(8), 36 (February 22, 2010).

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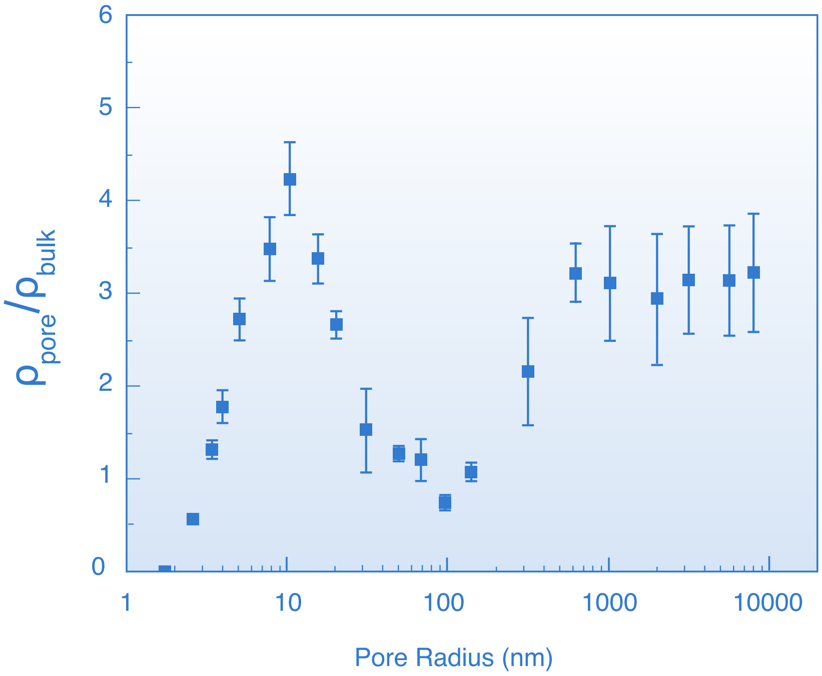

The variation of the ratio of CO_2 density in coal pores and in bulk as a function of pore size.